Comments on "Unusual Thermoelectric Behavior Indicating a Hopping to Bandlike Transport Transition in Pentacene"

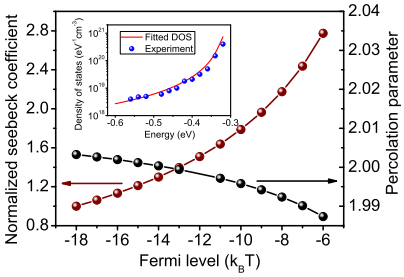
W. Chr. Germs, K. Guo, R. A. J. Janssen, and M. Kemerink [1] recently measured the temperature and concentration dependent seebeck coefficient in organic thin film transistor and found the seebeck coefficient increases with carrier concentration (corresponding to the gate voltage) in the low temperature regime. They further concluded that this unusual behavior was due to a transition from hopping transport in static localized states to bandlike transport, occurring at low temperature. This is obviously in contrast to the previous theoretical prediction because it is widely accepted that hopping transport is more pronounced at low temperature. We will discuss the reason for this unusual behavior here and suggest that the density of states function plays an important role in concentration dependent seebeck coefficient.

Note that, based on the percolation theory and hopping transport, the seebeck coefficient S could be calculated as [2, 3]

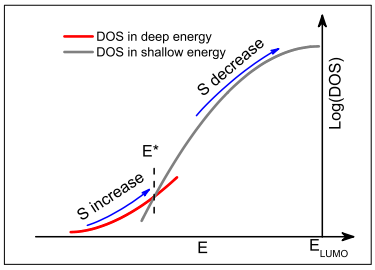
$$S = \frac{k_B}{e} \frac{\int \frac{E_i+E_j-2E_F}{2k_BT} g(E_i)\, g(E_j)\, dE_i dE_j d\mathbf{R}\theta(s_c - s_{ij})}{\int g(E_i)\, g(E_j)\, dE_i dE_j d\mathbf{R}\theta(s_c - s_{ij})}. \quad (1)$$

Where $g(E)$ is the density of states (DOS) at energy E, $s_{ij} = 2\alpha R_{ij} + \frac{|E_i-E_F|+|E_j-E_F|+|E_i-E_j|}{2k_BT}$ according to the hopping theory, and s_c is the critical percolation parameter [3]. In organic semiconductor, DOS is usually described as single Gaussian or exponential function, the seebeck coefficient in this situation is found decreasing with carrier concentration based on equation (1). However, DOS in organic semiconductor is very complicated and single Gaussian or exponential function can approximated only part of the density distribution and the different DOS function will affect the seebeck coefficient. For example, if we choose the DOS as function as $g(E) \propto \left(1 + (E_0 + \mid E \mid)^{-p}\right) (p > 0$, which shows good fitting with measured deep energy DOS for organic semiconductor [4](inset of Fig.1 (a)) including pentacene [5]), in this situation, both conductivity and seebeck coefficient increase with fermi energy as shown in Fig. 1 (a)(s_c decreasing means conductivity increasing and fermi energy is corresponding to carrier concentration or gate voltage).

Next, we want to interpret this behavior. In fact, the seebeck coefficient could be simplified as $\mid S \mid \propto \frac{dLog(\mu(E)g(E))}{dE}$ [6], it is very clear that the energy differential of the DOS affects the S-value. At high temperature, the transport path of carrier lies in the DOS for shallow energy ($E > E^*$), $dLog(DOS)/dE$ monotonically decreases with energy and the S-value decreases accordingly with concentration (carriers will occupy the higher energy with concentration increasing); however, at low temperature, the carrier transport path is in the deep energy states as shown in Fig.1 (b), if $dLog(DOS)/dE$ increases with energy, the S-value is no surprised to possibly increase with concentration. Certainly, the relation between μ and E should be also taken into account, as we have done in Fig. 1(a).Moreover,the same conclusion is reached if we substitute the DOS in Fig.1 (a) and transport energy model [7]into equation (1) in [1].



(a)



(b)

FIG. 1: (a) The calculated fermi level dependent percolation parameter s_c and normalized seebeck coefficient; Insert: Comparison between fitted (line) and measured DOS(symbols). (b) Schematic DOS-E model for this work.

Hence we conclude that, the seebeck coefficient increases with concentration in [1] might be attributed to the DOS shape in the low temperature, and this experiment could not prove hopping transport to be invalid in pentacene transistors.

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